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A STUDY OF THE LONG-TERM WEATHERING OF SUBMERGED AND OVERWASHED OIL

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SUMMARY

Progress in an on-going study is described of the long-term weathering phenomena which are experienced by heavy crude oils and residual fuels when present on a sea surface and subject to overwashing, evaporation, dissolution and photolysis. Experiments were designed and conducted to measure the increase in density of four oils (two heavy Californian crude oils, Cold Lake bitumen and a bunker fuel) as they were subjected to these weather processes. A novel experimental system for making these density measurements was devised. Experimental results were obtained and analysed. A mathematical model was developed and fitted to the data. It is concluded that the primary causes of increased density are evaporation of the more volatile and less dense components of the oil and incorporation of denser-than-water mineral matter into the oil. The effect of dissolution on density is negligible. It is hoped that the results of the mathematical model will assist in the elucidation of the conditions under which heavy oils become subject to permanent sinking in the marine environment.

Recommendations are made for future work, especially the development of protocols for determining the susceptibility of oils to density increase by evaporation and dissolution and the development of expressions describing the extent of overwashing and episodic sinking.

INTRODUCTION

The Phenomenon of Sinking

Conventional oils and petroleum products when spilled in the marine environment almost invariably float on the water surface and are subject to a number of processes including evaporation,

2.   Dissolution

Oil components are subject to dissolution, particularly as a result of overwashing by wave action. Again the more soluble hydrocarbons will preferentially dissolve. The preferential dissolution of the less dense lower molecular weight species, and especially the lower molecular weight aromatics may result in an increase in oil density.

3.   Photolysis

Photolytic processes can result in polymerization to form denser, higher molecular weight species. Photolysis may also cause the formation of free radicals which are suspectible to oxidation resulting in the formation of denser oxygenated species as peroxyl and hydroxyl radicals, alcohols, ketones, carboxylic acids and aldehydes.

4.   Attachment of foreign matter

The oil mass comes into contact with mineral matter such as diatomaceous material and biota which may become attached to the oil, or become incorporated into it, resulting in an increase in density. This process has been observed and reported by Wong et al. (1984) and may be responsible for oil sinking especially in areas of high suspended solids content, for example in relatively shallow near-shore waters, estuaries or during storms. One situation in which this process is very important occurs when viscous oil masses drift into the breaking wave region close to sandy shores. The oil drops, which may range from a few millimetres to a few centimetres in diameter may pick up sand particles, thus becoming denser. Eventually they may become incorporated into the beach, or if the tide is receding, they may drift out to sea and become partially or totally submerged, or sink to the bottom. Evidence was obtained from the "Nestucca" barge spill off the BC coast in late 1988 to the effect that collected oil contained an appreciable sand content and thus had been subject to this process (Fingas-personal communication, 1989).

5.   Water uptake

Finally, it is likely that most oils incorporate water both by dissolution and formation of water-in-oil emulsions thus causing an increase in oil density. In some cases, in which the

oils contain emulsion-stabilizing species, water volumetric contents as high 80 to 90% have been observed.

The Experimental Approach

A laboratory research program was designed to measure density increases over periods of approximately 20 days, of oils exposed to various weathering regimes including evaporation, dissolution, contact with solid materials and microbiota and photolysis. It was decided to use four oils of relatively high density and high viscosity. These were Cold Lake Bitumen (CLB), California Crude Oil API 11 (C11), Bunker C Fuel Oil (BC) and California Crude Oil API 15 (C15). These oils were subjected to physical-chemical property determinations and analysis by gas chromatography. A program of exploratory research was then undertaken to devise a system in which oils could be exposed to various weathering regimes and the density increases monitored using a relatively non-disturbing technique. This proved to be difficult, but after some trial and error an exposure measurement system was devised which it is believed gives as good results as is possible with the present state of knowledge and resources. A mathematical model is being developed to express or "fit" and correlate the density increases in a quantitative manner. The experimental results obtained are described briefly in this paper. It is hoped that ultimately this study will yield an equation for density variation with time which contains a minimum number of adjustable parameters which describes satisfactorily the observed experimental data. With appropriate caution the equation may have the potential to predict density increases of oils in marine environmental conditions.

EXPERIMENTAL

The four oils tested supplied by Environment Canada and the US Minerals Management Service are listed along with selected physical-chemical properties in Table 1. This table contains data kindly provided by M. Bobra. Table 2 gives information on the composition of these oils obtained by open column liquid chromatography under the defined conditions. Gas chromatograms are shown for the fresh oils in Figures 1 to 4. The oils were contacted with double distilled water and salt water consisting of 32 parts per thousand sodium chloride (NaCl) and the water soluble fraction subjected to analysis. California Crude 15 showed the presence of appreciable concentrations of lower aromatics having a total water solubility of approximately 26 mg/L in freshwater and 15 mg/L in salt water. Since the average solubility of these hydrocarbons is some

Table 1. Properties of Crude Oils and Residual Fuels

Property	California Crude No. 15.0	Bunker C Fuel Oil	California Crude No. 11.0	Cold Lake bitumen	temp.(°C)	reference
API Gravity	13.2	12.3	10.3	9.8	20	Environment Canada (EC)
Density (kg/m³)	990.7	994.1	996.8	1007.5	0	EC
	983.2	990.4	994.2	1004.9	5	EC
	980.2	986.7	991.5	1002.3	10	EC
	977.0	983.0	988.2	1000.2	15	EC
	973.5	978.8	985.2	996.8	20	EC
	968.1	971.2	977.9	985.1	22 ± 2	this work
	970.2	974.9	982.4	994.3	25	EC
	967.2	971.8	979.6	991.6	30	EC
Viscosity (cp)	6.4E3	1.4E6	2.2E5	>3.0E6	0	EC
	3.1E4	4.8E4	3.4E4	2.4E5	10	EC
Solubility (mg/L) d.d.H2O	25.7	4.23	11.3	0.26	22 ± 2	this work
salt H2O*	14.7	1.95	9.74	0.13	22 ± 2	this work

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*3.0 wt% NaCl in salt water

Table 2. Hydrocarbon Analysis by Open Column Chromatography

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	weight %			
	California Crude API 15.0	Bunker C Fuel Oil	California Crude API 11.0	Cold Lake bitumen
composition				
saturates	13.7	31.3	13.7	16.6
aromatics	36.4	45.7	29.8	39.2
asphaltenes	25.8	10.8	24.8	19.3
NSO compounds	24.1	12.2	31.7	24.9

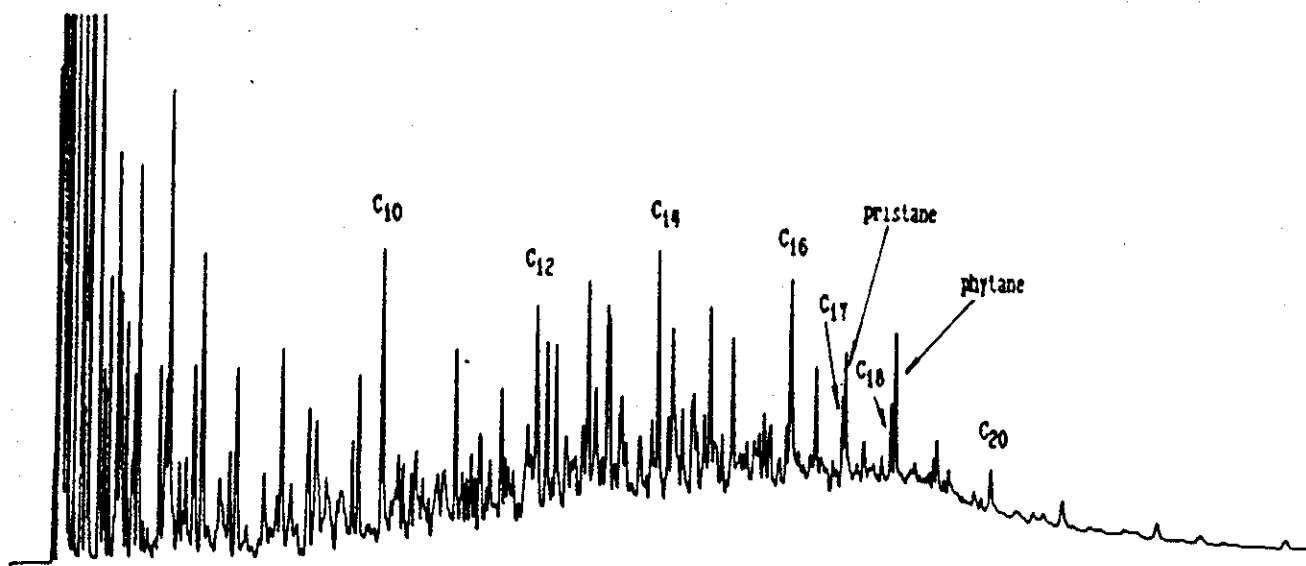
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Figure 1   Gas Chromatogram of fresh California Crude Oil (API 15).
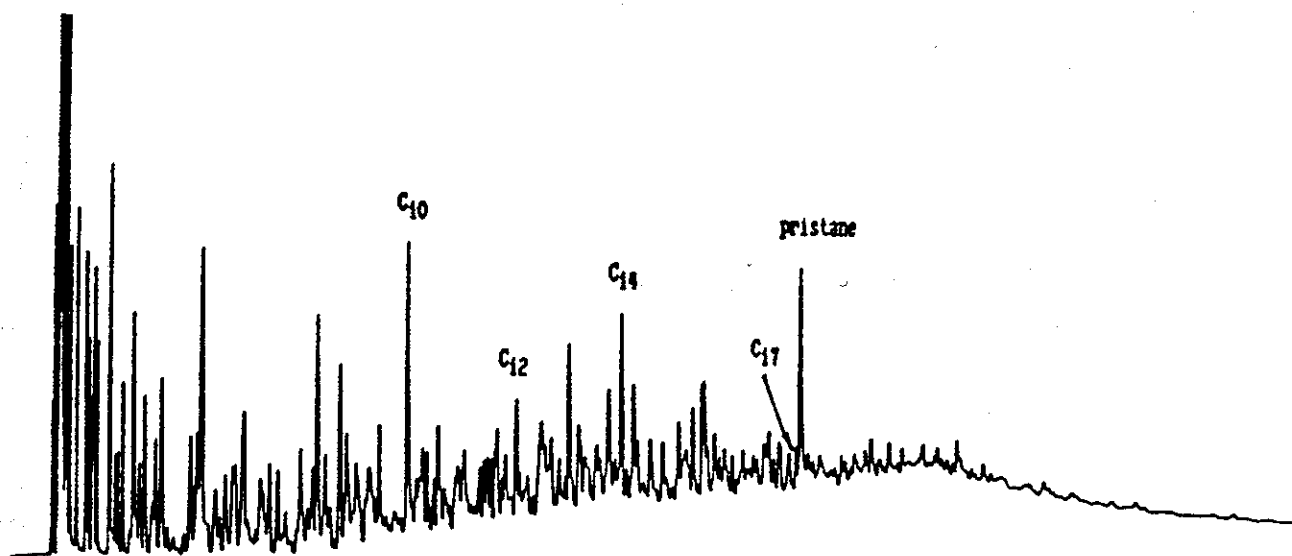

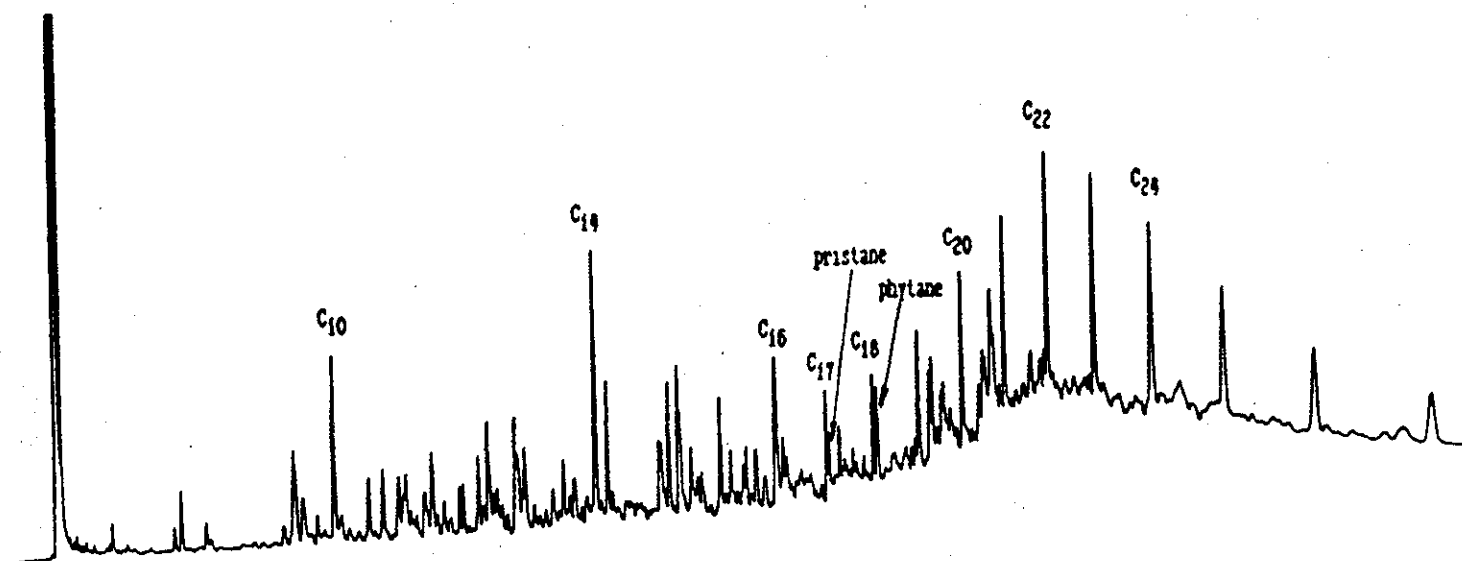Figure 2   Gas Chromatogram of fresh California Crude Oil (API 11).

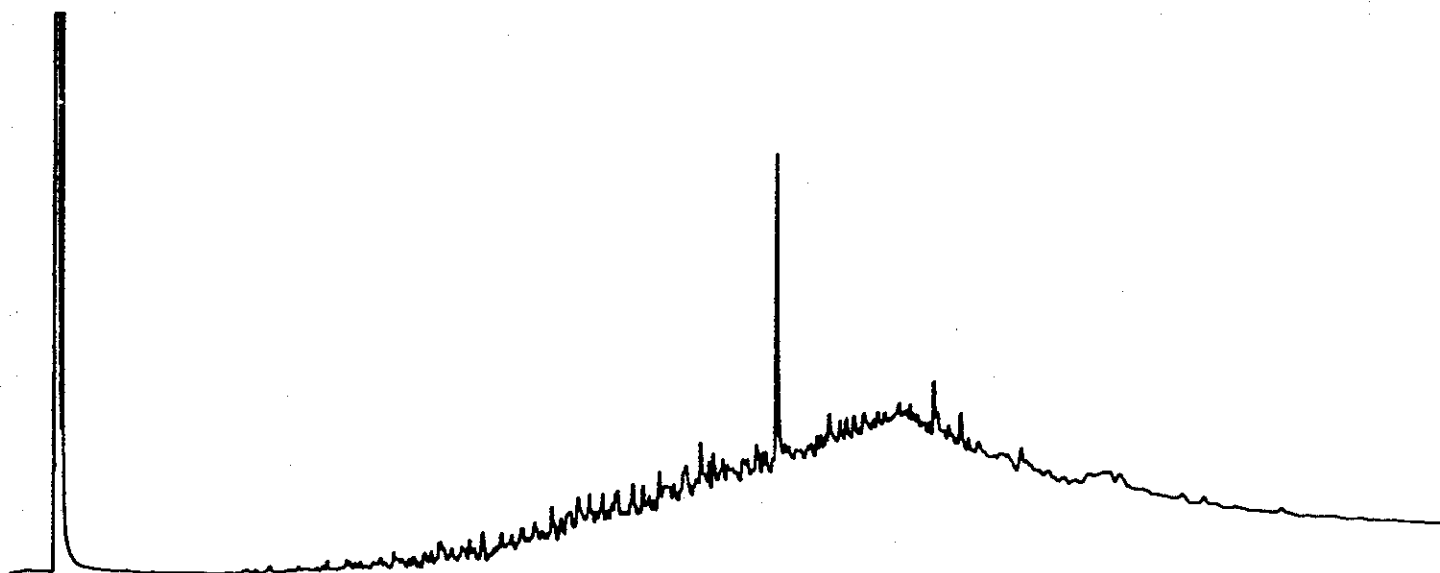Figure 3   Gas Chromatogram of fresh Bunker C Fuel Oil.

Figure 4   Gas Chromatogram of fresh Cold Lake Bitumen.

400 mg/L, it appears that this oil contains a mole fraction of these fairly soluble hydrocarbons amounting to 25/400 or 0.06 or approximately 6%. California Crude 11 had approximately half of this quantity. The Bunker C Fuel Oil had a very low concentration of aromatics presumably as a result of extensive distillation. Cold Lake Bitumen had only negligible contents of lower aromatics.

Density Determination

The system eventually adopted for exposure and density determination is illustrated in Figure 5. Disks were obtained of polyester mesh of diameter 6 cm made from PeCap polyester manufactured Tetko Inc. This mesh has an opening of 0.5 mm and a filament diameter of 0.3 mm. A number of mesh sizes and thread diameters were tested, however, this combination was found to be most suitable in that the oil was well retained by the mesh with a minimum of "dripping". Plastic mesh is preferable to metallic mesh because of its lower density.

The approach used to determine densities was basically the Archimedean principle of weighing the oil mass in air and in water, the difference being the buoyancy induced by displacement of the volume of water. Corrections were introduced for the presence of the mesh. The equation used (in units of kg and m^3) was:

$$\text{Density of oil } D_O = \text{Mass of oil } M_O / \text{Volume of oil } V_O$$

where
$$M_O = M_T - M_M$$
where M_T is the mass of oil plus mesh in air and M_M is the mass of the mesh,

and
$$V_O = V_T - V_M$$

where V_T is the total volume of oil plus mesh and is calculated from

$$V_T = (M_T - M_{TS})/D_W$$

where M_{TS} is the apparent mass or weight of the submerged oil plus mesh and D_W is the density of the water. $(M_T - M_{TS})$ is thus the buoyancy induced by the water.

V_M is the volume of the mesh which was determined by weighing the mesh in air and water.
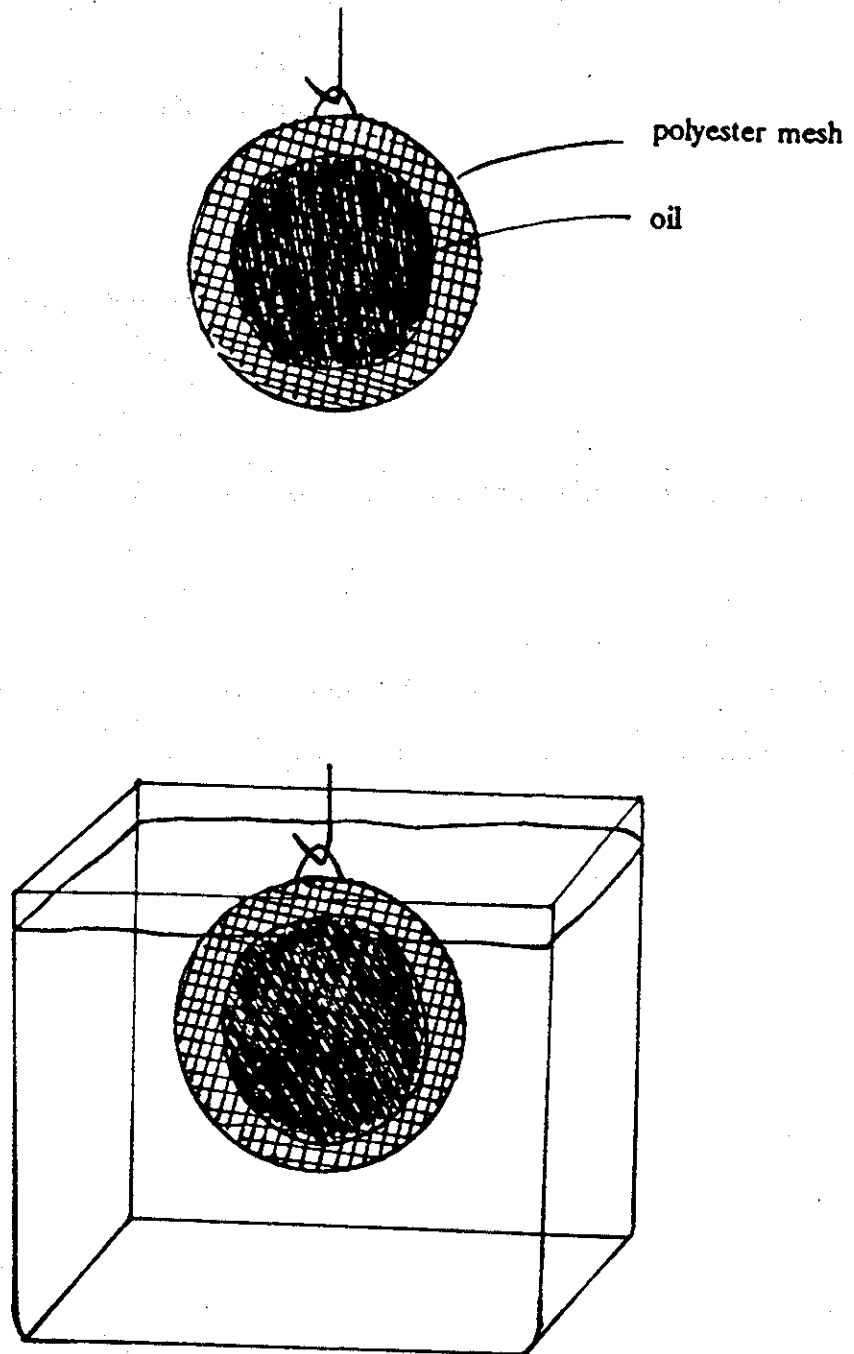
polyester mesh

oil

Figure 5   Diagram of experiment system in which oil-coated mesh disks are weighed in air and in water. The disk diameter is 6 cm.

Care was taken to remove all air bubbles from the oil and mesh during weighing in water and to minimize surface tension effects on the suspending filament. In the early stages of the work considerable effort was devoted to improving technique, accuracy and precision.

Usually, 0.5 to 1.0 g of oil was coated on to six mesh disks of 60 mm diameter with heat-sealed edges. This gave a reproducible and controlled area/volume ratio.

A Hewlett-Packard GC model 5700A equipped with a flame-ionization detector was used to analyze fresh and weathered samples of oil obtained from the oil weathering experiments. The column was 0.05 cm ID x 50 m long glass capillary column. The operating conditions were: the initial oven temperature was 50°C for 8 minutes and the oven temperature was programmed to 250°C at a rate of 5°C/min. The injection sample has a volume of 0.5 uL with a split ratio of 50:1, and peak areas recorded with a Shimadzu Chromatopac C-R1A integrator using the area normalization method.

For the column chromatographic separation approximately 1.5 g of oil was diluted in 100 mL of n-pentane. The mixture was filtered throuth a pre-weighed filter to remove the asphaltene content. The filter was dried in a heating compartment for 24 hours before being weighed again to determine the percentage weight of asphaltene.

The de-asphaltened oil was separated into three fractions: saturates, aromatics and polar compounds using the procedure described by Cook and Westlake (1976). A dual-phase colume packed with 1:1 ratio of silica gel and alumina was used. The silica gel (28-200 mesh) and alumina (type F-20, 80-200 mesh) were supplied by Sigma Chemical Co. The order of elution was as follows: saturates with pentane, aromatics with benzene, and then soluble polar compounds with a 1:1 mixture of benzene-methanol. The collected fractions were concentrated and later weighed to obtain the percentage composition of each fraction in the crude oils.

The following weathering experiments were conducted on the four crude oils:

- evaporation in the fumehood in the dark,
- evaporation in the fumehood with photolytic exposure,
- dissolution in a continuous flow of distilled water,
- dissolution in salt water,
- biodegradation,

- contact with suspended inorganic particles, and
- dissolution with photolytic exposure.

Evaporation

From initial tests, it was found that only a small fraction of oil (up to 20%) was retained on the disc when it was held stationary in air; therefore, a rotating device was devised which rotated (at a rate of 1.0 rpm) the oil-covered discs continuously between a horizontal and a vertical position. However, there was a small possibility of oil dripping off the discs during the first few days. The apparatus was placed in a fumehood that had a fairly high air flow. Two runs of the evaporation experiment were performed for 3 to 4 weeks with one at 19-20°C and the other at 22-24°C. Density measurements were taken after, 6, 24, 48, and 72 hours from the initial exposure for the second run because the greatest changes in density occur during the initial evaporation period.

The remaining experiments were conducted at 20°C ± 2°C.

Photolysis in Air

The source for photolysis was two fluorescent UVA-340 40-watt lamps which were mounted on standard light fixtures in the fumehood. The 48 inch fluorescent tubes were obtained from the Q-Panel Company. The lamp's emission was in the UV-A region with a small amount of UV-B. This is believed to be a satisfactory simulation of sunlight in the critical short wavelength UV region in the range 365 nm to 295 nm.

Oil samples on the discs were again circulated vertically on a rotating device.

Dissolution

Stainless steel hooks attached on to glass rods were used to hang oil-covered mesh disks vertically into a tank containing 27 L of distilled water. The disks were spaced apart at a distance of 2.5 cm. A constant daily flowrate of water was maintained with inflow of fresh water supplied by an overhead cylindrical tank. The disks were rotated 90° from the original position every two days for the first two weeks to prevent the oil from flowing off the disks and creating a slick on the water surface. Approximately 1.0 g of oil per disk was applied.

A second dissolution experiment used salt water instead of distilled water. Instant Ocean[R] (manufactured by Aquarium Systems) was used to provide the salt content which approximately simulates that found in sea water. Only 0.5 g of the oil was applied on each disc because of the high tendency for the oil to separate from the disk and float to the water surface. Half of the 7.5 L salt water was replaced weekly with a freshly-made solution of equal density.

Density measurements for both dissolution experiments were made weekly. However, before the densities of the oils could be determined, the oil-discs were dried on a rotating device in the fumehood. Inevitably this resulted in some dissolution.

Photolysis in Water

This apparatus was similar to the dissolution experiment except for the additional use of sunlight-simulation lamps. The UVA-340 lamps were angled such that more ultra-violet light was received by one side of the glass tank. After each weekly measurement, the disks from the two diffrent sides were manually interchanges so that each oil had the same light exposure.

Contact with Inorganic Particles

In the initial experiments purified bentonite powder (supplied by Fisher Scientific Co.) of 0.1 wt% in distilled water was used to expose the crude oils to suspended mineral matter. This mixture had to be continously stirred at a moderate speed to produce a uniform suspension of particles throughout the 7.5-L tank. High stirring speeds caused the oil-coated disks to collide with each other.

Before the oil densities can be determined, the discs were initially immersed in distilled water in an attempt to displace the bentonite particles from the exposed mesh openings. The oil covered disks were then dried on the rotating device for about 40 minutes.

After these initial experiments a more comprehensive series of experiments was undertaken exposing the oils to a series of mineral materials, including:

- Pottery clay purchased from a local hobby shop
- Riverbed clay obtained from a river near Whitevale, Ontario
- Kaolinite obtained from the Geology Department, University of Toronto

- Diatomaceous earth (Fisher)
- Soapstone, i.e. talc, obtained by grinding a piece of soapstone obtained at a hobby shop for carving purposes

Soapstone was used because it is reputed to be very "hydrophobic" and may thus be unusually susceptible to oil attachment.

MATHEMATICAL MODEL

The general aim of the mathematical model is to provide a quantitative description of the change in density of the oil as a function of exposures such as evaporation, dissolution, contact with solid materials and photolysis. This provides a method by which the experimental data may be converted into parameter values which can be used to correlate the data and possibly predict the effect of exposure to several density-increasing regimes. No previous models exist describing these density increases, thus the development described here is novel and undoubtedly will be the subject of improvement as a result of scrutiny and testing against future experimental data. The approach used should thus be regarded as exploratory in nature.

In the interest of brevity only the general nature of the final correlating equations in presented here. The forthcoming project report will contain a more detailed derivation and justification.

Evaporation

The oil is treated as consisting of three components, a volatile fraction (1), a less volatile fraction (2) and an involatile residue (R). It can be shown that such a mixture will increase in density D according to an equation of the form shown below in which D_R is the residue density and E_1 and E_2 are the products of the volume fraction of components 1 and 2 and the density difference (D_R-D_1) and (D_R-D_2). Two rate constants k_1 and k_2 are introduced.

$$D = D_R - E_1 \exp(-k_{E1}t) - E_2 \exp(-k_{E2}t)$$

This can be rearranged to give an expression for the density increase from that of the original oil density $(D_R - E_1 - E_2)$ namely,

$$\Delta D_E = E_1(1 - \exp(- k_{E1}t)) + E_2(1 - \exp(-k_{E2}t))$$

Further, rather than report k_1 and k_2 as reciprocal times (e.g. 0.01 h^{-1}) it is more meaningful to report them as $1/T_1$ and $1/T_2$ where T_1 and T_2 are characteristic times, e.g. 100 hours.

Dissolution

A similar analysis can be conducted for dissolution yielding an equation for density increase as a function of dissolution which is identical in structure to that for evaporation, but only one component is needed

$$D = D_R - F_1 \exp(- k_{D1}t)$$
or
$$\Delta D_D = F_1(1 - \exp(- k_{D1}t))$$

If the components which evaporate are not those which dissolve then the equations for evaporation and dissolution could be added and evaporating and dissolving components could be identified separately. In reality this is unlikely to apply because the components which dissolve will tend to be those of lower molecular weight which probably are also subject to evaporation, i.e. E_1 and F_1 are equivalent. It is therefore probably more reliable to add the rate constants for evaporation and dissolution and apply them to the same component thus giving an equation of the form shown below for two components

$$D = D_R - E_1 \exp(- (k_{E1} + k_{D1}) t) - E_2 \exp(- (k_{E2})t)$$
or
$$\Delta D_{DE} = E_1(1 - \exp(- (k_{E1} + k_{D1})t) + E_2(1 - \exp(- k_{E2}t))$$

Photolysis

For photolysis we postulate that some of the residual oil experiences a density increase thus the overall density of the oil increases according to an equation of the form.

$$D = D_R(1 + Gt)$$

where G is a fitted constant. An alternative and possibly preferable expression is

$$D = D_R + D_P(1-\exp(-k_P t)) = D_R + \Delta D_P$$

where ΔD_P is a density increase attributable to photolysis and k_P is a rate constant.

In practice it is likely that some part of the component 1 will also be subject to photolysis. However, it is probably impossible to discriminate this from the residue using experimental data thus we prefer to assume that photolysis only applies to the residual material. Some justification of this approach is obtained by noting that photolysis occurs at the surface of the oil which is most severely depleted by evaporation and dissolution.

Attachment of Foreign Matter

When foreign matter such as clay, microorganisms or diatomaceous matter becomes attached to the oil the bulk density of the oil will increase according to the equation

$$D = ZD_F + (1 - Z)D_O$$

where Z is the volume fraction of foreign matter of density D_F and D_O is the oil density. This can be rearranged to the more convenient form below by expressing density as a function of the difference between the solid density and the oil density and the density.

$$D = D_O + Z(D_F - D_O)$$

thus
$$\Delta D_F = Z(D_F - D_O)$$

As is discussed later there appears to be a non linear density increase with an initial rapid uptake followed by a slower uptake. This may be due to a viscosity increase or the coverage of the surface by mineral matter. A convenient correlating expression is

$$Z = Z_F(1-\exp(-k_M t))$$

where Z_F is the final value of Z and k_M is a rate constant.

Overall Density Equation

Combining the expressions for evaporation dissolution, photolysis and attachment of foreign matter, the density of an oil mass is postulated to be described by the equation given below which contains adjustable parameters for the various processes. Examination of the magnitude of the parameters will show which of the processes are important and the rates of the density increase which can be expected

$$D = D_O + \Delta D_{DE} + \Delta D_P + \Delta D_F$$

The key problem is to obtain values of the parameters E_1, E_2 (alternatively F_1 and F_2), k_{E1} k_{D1}, k_{E2}, G, Z_F and k_M. An expression is being included to allow for separate exposure times to dissolution evaporation and photolysis to be included depending on the overwashed state of the oil. If this can be accomplished it will result in a relatively simple and easily understandable expression for oil density increase.

Evaporation vs. Dissolution

Finally, a theoretical analysis was undertaken to explore the relative importance of evaporation and dissolution as removal processes contributing to density increases. It was concluded that only those hydrocarbons with vapour pressures exceeding approximately 0.04 Pa (approximately that of hexadecane) will evaporation be significant in about a week. Similarly only hydrocarbons (or other chemicals) with solubilities exceeding 1 g/m³ (approximately that of phenanthrene) will dissolve appreciably.

Hydrocarbons which have vapor pressures below 10^{-2} Pa or solubilities below 1 g/m³ will be substantially retained by the oil and are unable to migrate into air or water because of the very low concentrations which they can establish in these receiving phases.

The alkanes to about C_{16}, the monoaromatics, the naphthalenes, the three membered PAHs and polar "hydrocarbons" containing O, N or S atoms are thus candidates for loss by evaporation or dissolution. The others are probably destined to remain in the oil. A consequence of this analysis is that it may often be fruitless to test the oil phase for evidence of loss of these chemicals, rather they should be sought in the "receiving" phases of air or water, i.e. the water solubility or

partial pressure of these chemicals should be measured as indicators of potential for migration from oil and thus for causing density increases.

RESULTS

Magnitude of Density Increases for Sinking

The data in Table 1 suggest that to reach a density of 1024 kg/m³ the oils must increase in density by the following approximate amounts at 10°C and 22°C.

	10°C	22°C
California 15	44	56 kg/m³
California 11	32	53 kg/m³
Bunker C	37	46 kg/m3
C.L. Bitumen	22	29 kg/m³

We are thus concerned with density increases in the range 20 to 60 kg/m³ which, if achieved by a single process or combination of processes could result in sinking, depending on the oil, the water and the prevailing temperature.

Evaporation

The first series of evaporation tests lasted for 21 days and showed that the oil density was increasing with time and served to confirm that the experimental method was valid. As a result of experience in this series, the number of replicates was increased from 3 to 5 and additional measurements of oil density were made early during the evaporation period because there was clearly a rapid increase in oil density during the first day. The second series of evaporation experiments yielded improved accuracy and a smaller standard deviation. The results for the four oils during this series are given in Figure 6. All oils showed a density increase during the first day presumably because of loss of volatile material. The Bunker C oil showed a relatively small increase presumably as a result of loss of volatile material during distillation. The Cold Lake
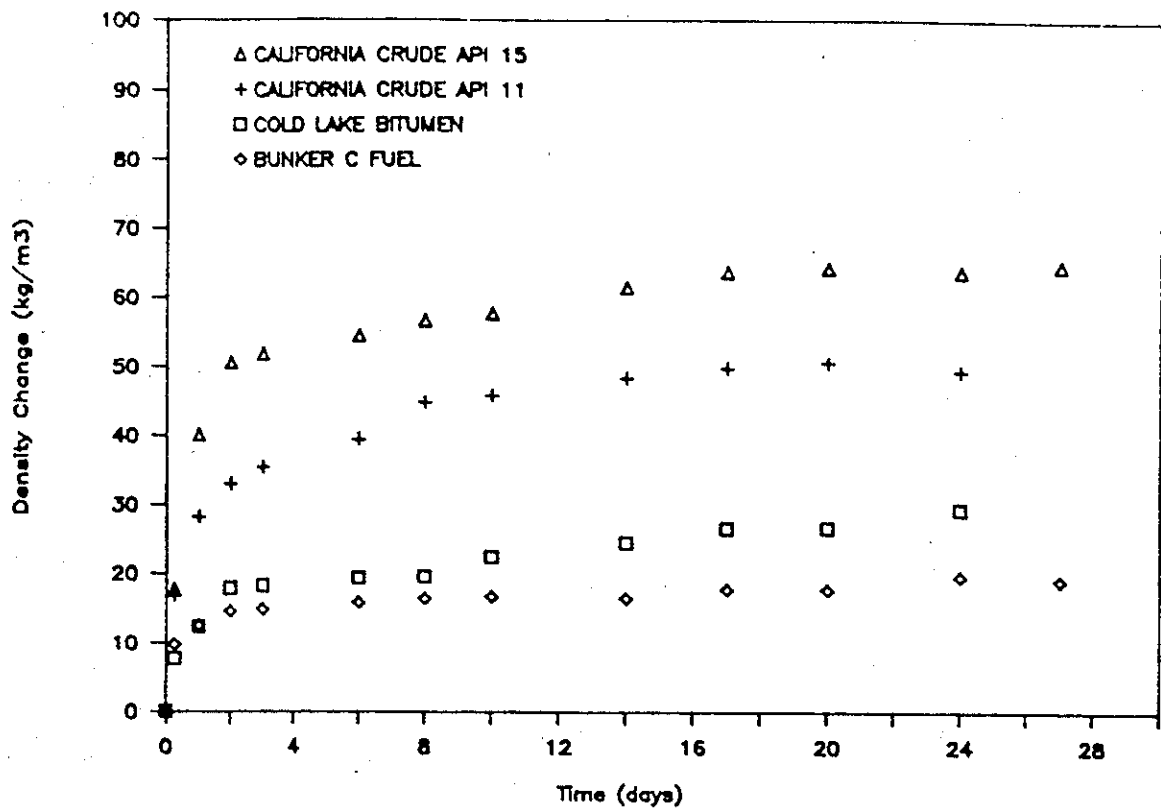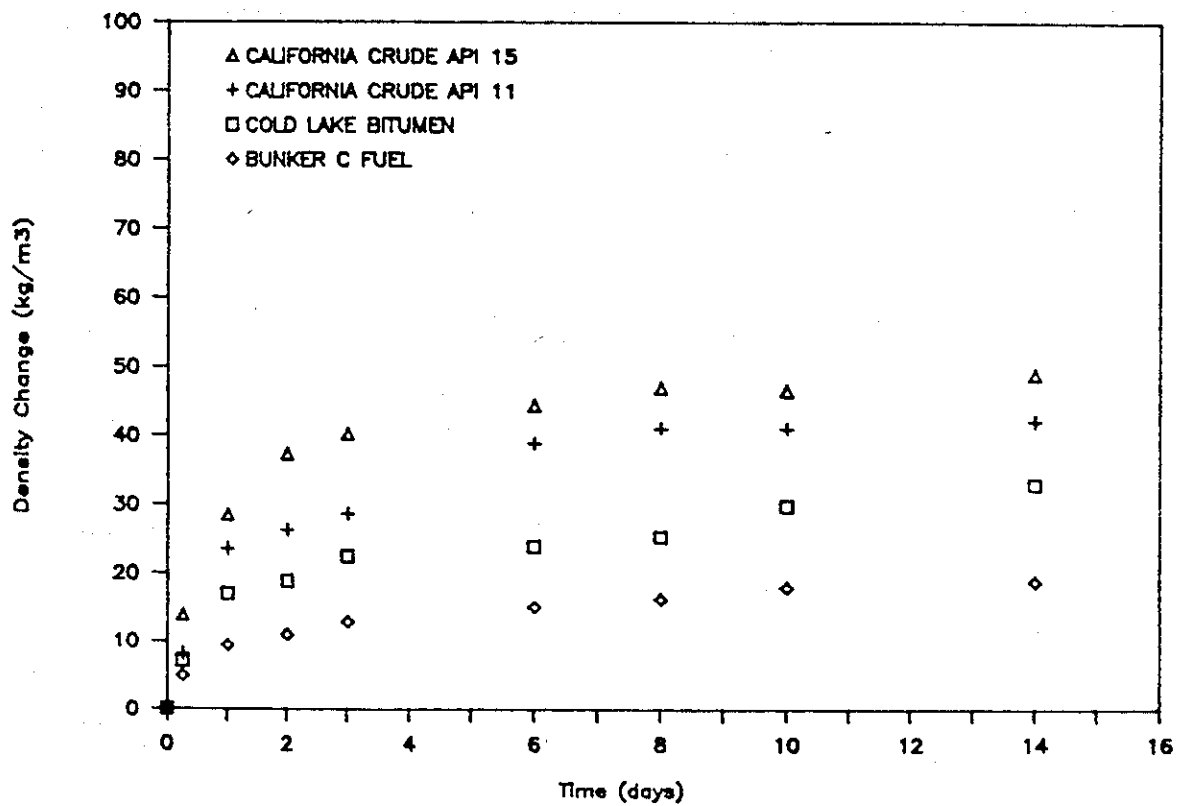
Figure 6.   Evaporation

Figure 6. Evaporation

Legend:
△ CALIFORNIA CRUDE API 15
+ CALIFORNIA CRUDE API 11
□ COLD LAKE BITUMEN
◇ BUNKER C FUEL

X-axis: Time (days)
Y-axis: Density Change (kg/m3)

Figure 7.   Photolysis in Air

Figure 7. Photolysis in Air

Legend:
△ CALIFORNIA CRUDE API 15
+ CALIFORNIA CRUDE API 11
□ COLD LAKE BITUMEN
◇ BUNKER C FUEL

X-axis: Time (days)
Y-axis: Density Change (kg/m3)

bitumen also showed a fairly small increase in density. The two crude oils showed larger density increases and there was a continual increase in density after three or four days.

Examination of the curves suggest that accurate description of density increase require the incorporation of at least three components in the system, i.e. two components which evaporate and a residue. The first component appears to evaporate with a time constant of the order of two days or 50 hours and the second one with a time constant of approximately 16 days or 400 hours. The two crude oils, C11 and C15, eventually display densities approaching that of sea water.

The estimated parameter values are as shown below.

Evaporation Parameters (units of hours, kg and m^3)

Oil	E_1	k_1	E_2	k_2	D_R
C11	38	1/50	15	1/400	1030
C15	51	"	13	"	1026
CLB	20	"	10	"	1014
BC	16	"	4	"	989

A note of caution is appropriate when interpretating of these results. The experimental technique is believed to be valid as a means of detecting density increases. The technique suffers from appreciable error in determining absolute densities because of the errors introduced in weighing and subtracting mesh masses and volumes. Occasionally a small amount of oil would float from the mesh surface thus confounding the density determination. It is possible that water dissolved in the oil thus affecting its weight in air, but not its weight in water. A compromise had to be made between prolonged drying with excessive evaporation and short drying with risk of retained water. Emphasis should be placed on the trends in relative density, not on absolute density.

Comparison of these parameter values suggests that the two crude oils are very susceptible to sinking, the C.L. Bitumen less so and the Bunker C is unlikely to sink by evaporation alone.

Evaporation Plus Photolysis

The effect of photolysis was generally to cause an increase in density beyond that of the evaporated oils, suggesting that photolysis either enhances evaporation (possibly by increasing the surface temperature of the oil) or results in formation of denser oil species. It was of course impossible to study photolysis in air in the absence of evaporation thus the approach taken was to calculate the increase in density of the photolyzed oil attributable to photolysis beyond that which occured for the second evaporation experiment and attribute that incremental increase in density to photolytic processes. For example, for CLB and CB that increase corresponds to a density increment of about 5 kg/m³ at 14 days or 336 hours. For C11 and C15 oils, the increase in densities attributable to photolysis was judged to be within the range of experimental error and no definite conclusion can be reached that photolysis causes an additional increase in oil density.

Fitting the data to the model suggests that the following values can be used.

Photolysis Parameters

Oil	$G\ (h^{-1})$
C11	0
C15	0
CLB	1.5×10^{-5}
BC	1.5×10^{-5}

Dissolution

Experiments were run in parallel using fresh deionized distilled water and using salt water. The oil was not exposed to light except during the density measurements and the water was changed periodically to remove any components which had dissolved. The experiments ran for 42 days and showed a small increase in density. The variation in density was quite erratic during these experiments. This is partly due to some difficulties experienced experimentally in which there may have been loss of some of the oil from the meshes during the exposure. It appears that the crude

oils show a more significant increase in density probably as a result of the presence of more soluble lower molecular weight material. The density increase is in the range 24 to 31 kg/m³ for the crude oils and is about 15 kg/m³ for the fuel oils.

Fitting a one-dissolving component model gives the parameters below.

Dissolution Parameters

Oil	Fresh Water		Salt Water	
	F_1	k	F_1	k
C11	24	1/250	40	1/400
C15	31	1/250	70	1/400
CLB	15	1/250	20	1/400
BC	15	1/250	20	1/400

The most notable feature of the dissolution effect is its slowness (i.e. low k_1) relative to evaporation. Much of this density increase is believed to be due to evaporation.

The salt water results showed a greater increase in density especially for the crude oils. This was not expected and the reasons for it are unknown. It seems unlikely, but it is not impossible, that the oil picks up salt possibly through the formation of sodium salts of carboxylic and phenolic acids.

Attachment of Suspended Matter

Two series of experiments were taken investigating the attachment of suspended solid matter to the oils. The initial results for clay demonstrated a density increase of the order of 80 kg/m³. The second series of experiments yielded more accurate data and are discussed in more detail.

Figure 9 gives some typical density increases for selected mineral materials. In these tests the densities increased considerably, i.e. by 60 to 70 kg/m³ often reaching a value higher than that of seawater. There did not appear to be any strong influence of mineral type. The principal
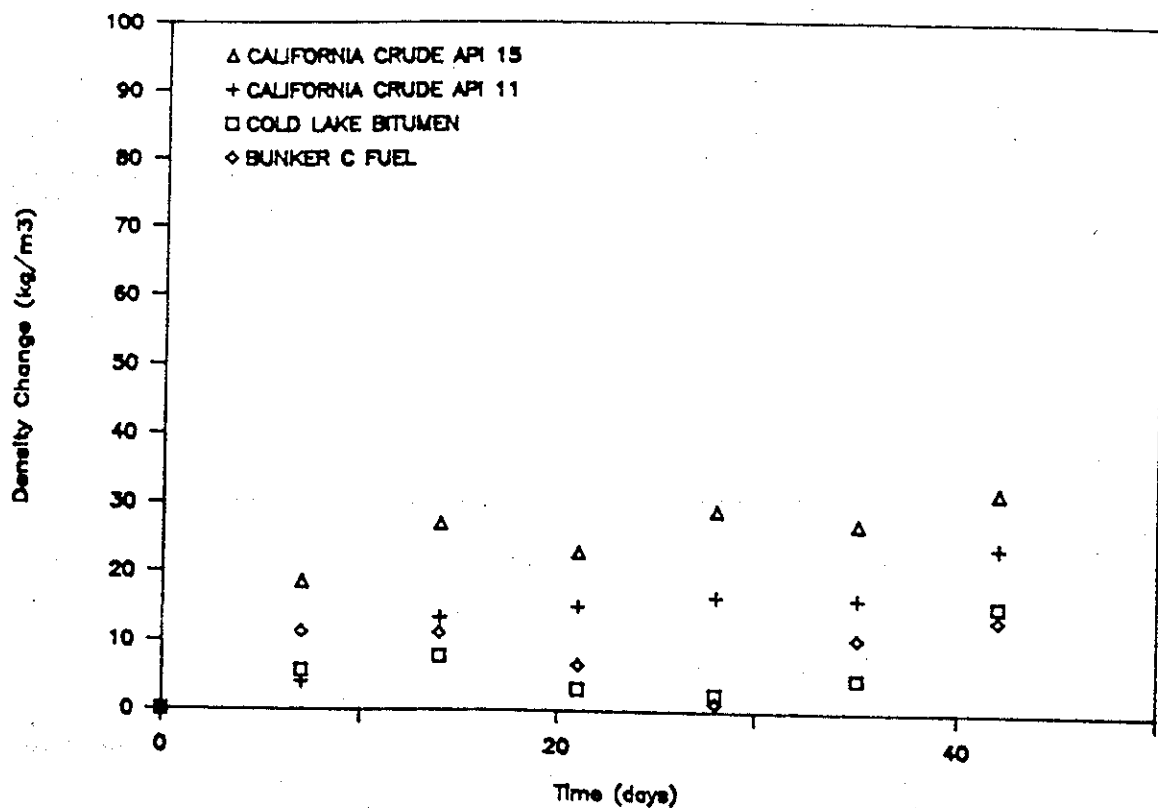
Figure 8. Dissolution

Legend:
- △ CALIFORNIA CRUDE API 15
- + CALIFORNIA CRUDE API 11
- □ COLD LAKE BITUMEN
- ◇ BUNKER C FUEL

Y-axis: Density Change (kg/m3)
X-axis: Time (days)

Figure 9. Incorporation of Particles
California Crude Oil API 15

Legend:
- □ POTTERY CLAY
- + RIVERBED CLAY
- ◇ KAOLINITE
- △ DIATOMACEOUS EARTH
- × SOAPSTONE
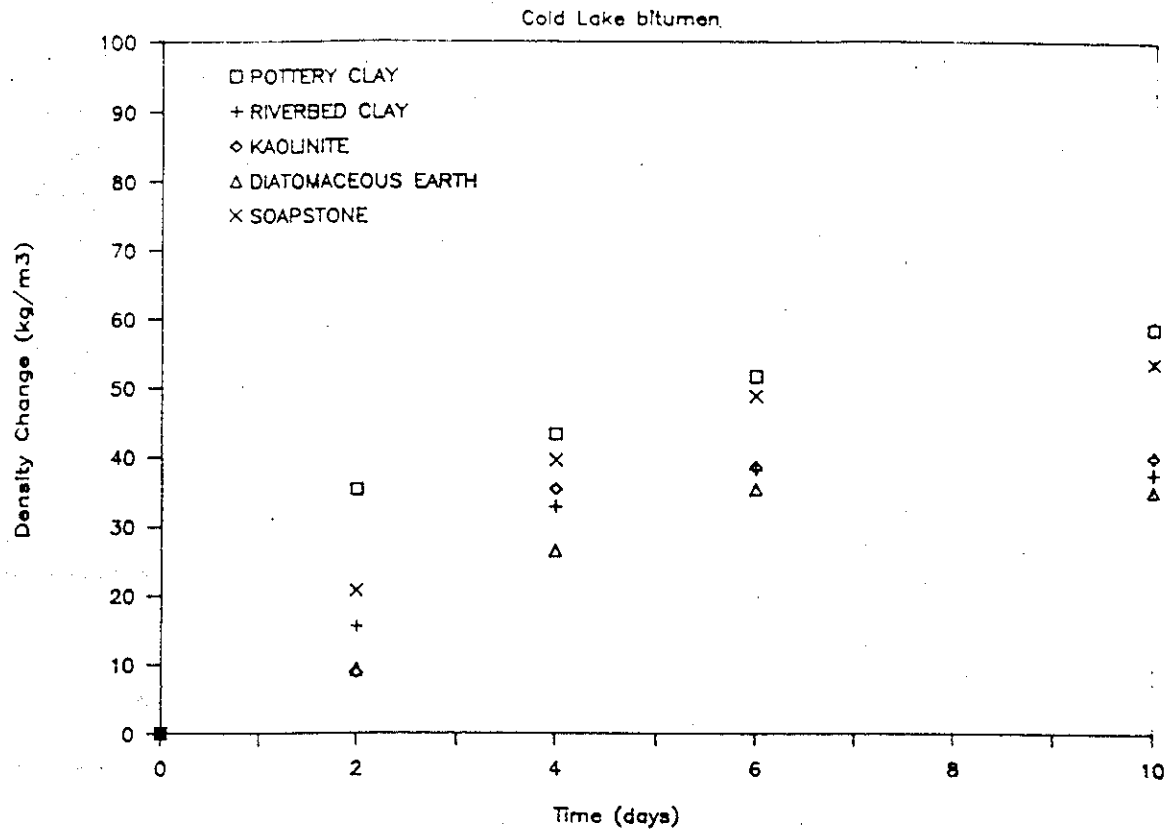
Y-axis: Density Change (kg/m3)
X-axis: Time (days)
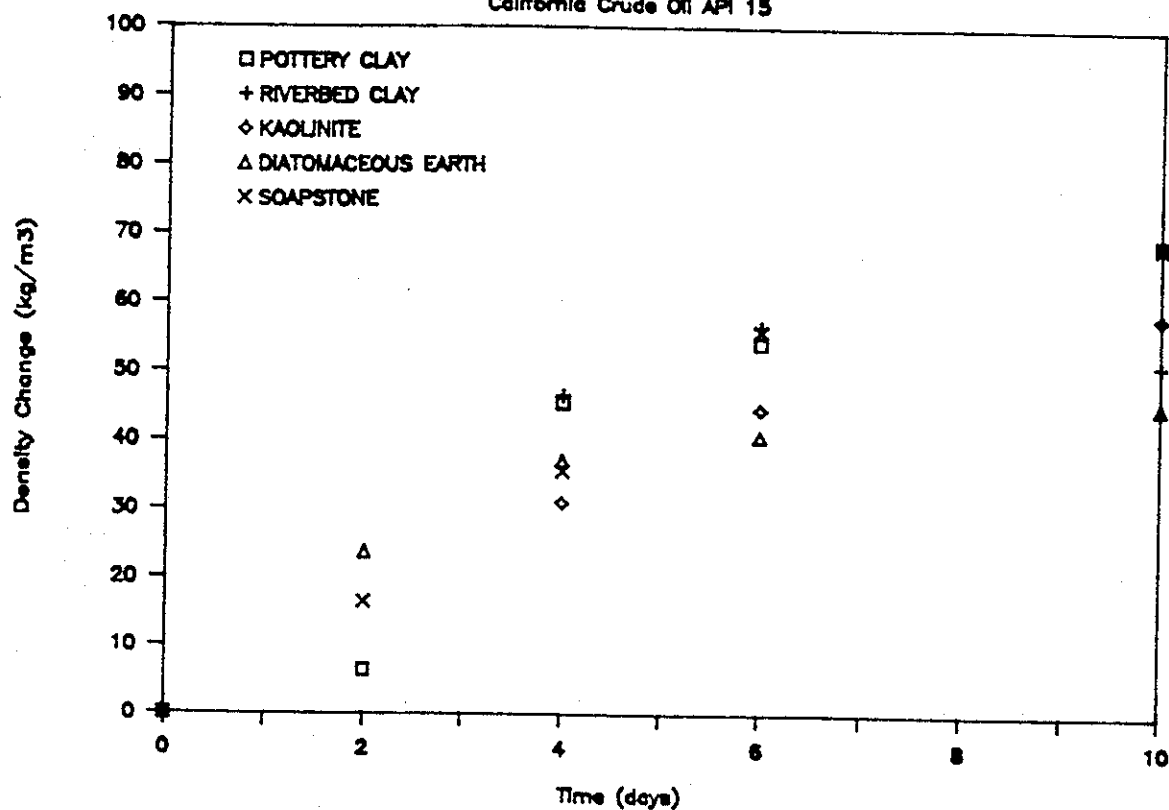
Figure 10. Incorporation of Particles

Cold Lake bitumen

differences in behaviour between mineral types is attributable to differences in suspended solids contents. Some minerals (notably talc) proved to be difficult to maintain in suspension. Various approaches were tested in an attempt to standardize the solids concentration but this proved to be a formidable experimental task.

DISCUSSION

Susceptibility to Sinking

The results indicate that the primary causes of oil density increase are (in order of decreasing magnitude) evaporation, incorporation of solid material, photolysis and dissolution. Conditions can arise in which singly or in combination will cause the oil to achieve a density exceeding that of sea water. Evaporation is particularly important for the crude oils which still retain some of the lower molecular weight hydrocarbons which are fairly volatile.

It is clear that the magnitude of the density increases attributable to evaporation alone or incorporation of solid material alone are sufficient to cause sinking in exposure times relevant to oil spill countermeasures responses. Evaporation will be delayed by overwashing, but it is believed that many of the compounds may dissolve then evaporate, thus overwashing does not necessarily "shut off" evaporation. It is difficult to extrapolate these results to oceanic conditions because of uncertainties about overwashing and solids concentrations, but the results strongly suggest that sinking will occur for heavy crude oils.

Test Protocols

The results obtained in this study are of course specific to the oils which were tested. However, it is believed that for other oils similar parameter values probably apply. It is possible that the experimental approach used here could be used to establish a protocol for the assessment of likely submergence behavior of specific oils. The oil characteristic which is most variable is probably the density increase attributable to evaporation. This can be relatively readily ascertained by exposing a volume of oil to evaporation in a wind tunnel or fume hood under conditions of known wind speed and film thickness. The oil can then be collected and its density measured. Alternatively distillation under controlled temperature conditions could be used.

An attractive alternative would be to "strip" a sample of oil with a slow nitrogen stream at controlled temperature conditions and collect the evaporated hydrocarbons by cryogenic trapping. This would ascertain the content of hydrocarbon which has the potential to evaporate. A similar approach could be used for dissolved hydrocarbons using a "generator column", but trapping the dissolved hydrocarbons from the eluate, possibly in an extracting solvent. These techniques are potentially much more sensitive than looking for changes in composition of the source oil. It is recommended that these approaches be investigated.

Oceanic Phenomena

It is suspected that oil present in the near-surface region is subject to a "self-regulating" mechanism of density increase which will tend to cause it to adopt a density similar to that of the sea water. Evaporation will cause a density increase but only when the oil mass is exposed to air. There will also be active photolysis during daylight resulting in the formation of denser and more soluble hydrocarbons. There is often an accumulation of solid material at the turbulent water surface which will cause a further density increase. In total these processes will induce the oil to become denser, then sink. If the oil then passes into sea water of lower density it may be subject to sinking episodes and reach the benthic region. It is thus not surprising that heavy oils when exposed to marine environmental conditions often vanish from the sea surface for prolonged periods only to reappear in distant locations. Once submerged the oil may "stabilize" and be subject to only slight density changes.

The process of water in oil emulsion formation or "mousse" formation may also serve to increase the oil density, but in principle it is impossible for this process to cause the density to increase beyond that of sea water. Indeed for oils which have a density exceeding that of sea water, "mousse" formation will reduce the density.

A process which has not been considered in this work is that of dissolution of water in oil which may also cause a density increase approaching that of sea water. The magnitude of this effect is not known but it is believed to be slight.

A compelling case can be presented for subjecting fuel oils or crude oils which are high in density to a rigorous determination of submergence characteristics in order that on-scene response groups can be warned about the probability of the oil displaying submergence behavior.

Mathematical Modelling

This study has clarified the role of mathematical models as a tool for addressing these phenomena. It is suggested that two models are needed.

First is a density model in which appropriate oil property data are combined with information about exposure to evaporation, dissolution, photolysis and solid matter to yield estimated density differences between oil and water. The model presented earlier could form the basis of such a capability.

Second is a model describing the resulting behaviour of the oil. It is erroneous to suggest that oil floats until its density reaches that of seawater, then it sinks. In reality the submergence phenomena are more continuous. Buist and Potter (1987) have suggested correlations for oil "blob" size, the extent of overwashing and depth of penetration into the water column and the fraction of the oil which is submerged at any given time. Such a model gives the information required by on-scene response personnel.

Interestingly, it is likely that the two models are interdependent because evaporation rate is influenced by extent of submergence, thus in principle a combined model may be required.

CONCLUSIONS

It is believed that this exploratory study has elucidated the dominant processes causing oil density increase and will lead to a suggested protocol for a density increase assessment and a mathematical procedure for characterising these processes. This procedure could be incorporated with relatively little effort into existing oil spill models used for environmental assessment or for on-scene response purposes. Clearly further work is desirable to investigate the role of photolysis, better characterize evaporation process, study a variety of solid phases under various concentration conditions and develop appropriate mathematical models to aid those responsible for on-scene response.

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REFERENCES

Buist, I.A. and Potter S.G. 1987. Oil Submergence. Spill Technology Newsletter, July-September 1987, pp. 65-82.

Clark, B., Parsons, J., Yen, C., Ahier, A., Alexander, J. and Mackay, D. 1987. A study of factors influencing oil submergence. Report EE90, Environment Canada, Ottawa.

Cook, F.D. and Westlake, D.W.S. 1976. Biodegradability of Northern Crude Oil. Department of Indian Affairs and Northern Development. Report No. QS-8116-000-EE-A1.

Juszko, B.A. and Green, D.R. 1983. Sinking of Oil: Water Density Considerations. Spill Technology Newsletter, March-April 1983, pp. 22-26.

Lichtenthaler, R.G., Hoag, W.R. and Mill, T. 1989. Photooxidation of probe compounds sensitized by crude oils in toluene and as an oil film on water. Environ. Sci. Technol. 23, 39-45.

Mackay, D. and McAuliffe, C.D. 1988. Fate of hydrocarbons discharged at sea. Oil and Chemical Pollution 5, pp. 1-20.

Mackay, D. 1987. Formation and Stability of Water in Oil Emulsions. Report EE93, Environment Canada, Ottawa.

Mackay, D. and Shiu, W.Y. 1981. A Critical Review of Henry's Law Constants for Chemicals of Environmental Interest. J. Phys. Chem. Ref. Data 10, 1175-1199.

Meyers, P.A. and Oas, T.G. 1978. Comparison of associations of different hydrocarbons with clay particles in simulated seawater. Environ. Sci. Technol. 12, pp. 934-937.

Meyers, P.A. 1972. Association of fatty acids and hydrocarbons with numeral particles in sea water. PhD thesis, University of Rhode Island, Dept. of Oceanography, University Microfilms 73-16739, Ann Arbor, MI.

Seakem Oceanography Ltd. 1986. Oceanographic conditions suitable for the sinking of oil. Report EPS 3/SP/2, Environment Canada, Ottawa.

SL Ross Environmental Research Ltd. 1987. The transient submergence of oil spills: tank tests and modelling. Report EE96, Environment Canada, Ottawa.

Wilson, D., Poon, Y.C. and Mackay, D. 1986. An exploratory study of the buoyancy behaviour of weathered oils in water. Report EE85, Environment Canada, Ottawa.

Wong, C.S., Whitney, F.A., Cretney, W.J., Lee, K., McLaughlin, F., Wu, J., Fu, T. and Zuang, D. 1984. An experimental marine ecosystem response to crude oil and corexit 9527, Part I. Fate of chemically dispersed crude oil. Marine Environ. Res. 13, pp. 247-263.